Ideal Gas Thermodynamic Properties of Propanone and 2-Butanone

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The ideal gas thermodynamic properties (C_p°, S°, $H^\circ - H_0^\circ$, $(H^\circ - H_0^\circ)/T$, $-(G' - H_0^\circ)/T$, ΔHf°, ΔGf°, and log Kf) for propanone and 2-butanone in the temperature range from 0 to 1500 K and at 1 atm were calculated by statistical mechanical procedures, using rigid-rotor and harmonic-oscillator approximations. The internal rotation contributions to thermodynamic properties were evaluated by use of a partition function formed by summation of internal rotation energy levels. The calculated heat capacities and entropies are in agreement with the available experimental values.

Key words: 2-butanone (methyl ethyl ketone); enthalpy; entropy; equilibrium constant of formation; Gibbs energy of formation; heat capacity; ideal gas thermodynamic properties; internal rotational barrier height; propanone (acetone); torsional frequencies.

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1. Introduction

Propanone (acetone, CH_3COCH_3) and 2-butanone (methyl ethyl ketone, $CH_3COCH_2CH_3$), as the two simplest aliphatic ketones, are key compounds for this homologous class of substances. Their statistical thermodynamic properties in the ideal gaseous state were reported in recent years by several investigators [1, 2, 3, 4, 5].[1] Unfortunately, due to incomplete and less than reliable input data on molecular and spectroscopic parameters, it was found necessary to estimate certain constants. Recently, more complete and reliable information has become available on the structure, vibrational assignments, and torsional frequencies for these two species. This information, coupled with improved procedures for estimating internal rotational contributions, permits us to reevaluate the ideal gas thermodynamic properties for the temperature range from 0 to 1500 K and at 1 atm.

All calculations in this work are based on the 1973 Fundamental Physical Constants recommended by the CODATA Task Group [6] and on the 1973 Atomic Weights: C = 12.011, H = 1.0079 and O = 15.9994. For conversion of the calculated results to SI units, the values 1 cal = 4.184 joules and 1 atm = 101325 Nm^{-2} should be used.

Propanone has two CH_3 groups, whereas 2-butanone has three tops, two CH_3 and one C_2H_5 group. These characteristic groups of atoms by rotating around the C—C bonds produce internal rotational contributions. The contributions of each internal rotational degree of

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[1] Numbers in brackets indicate literature references in section 6.

freedom to the thermodynamic properties of propanone and 2-butanone were calculated by use of partition functions formed by summation of the internal rotational energy levels, as described previously [8]. The results were added to the contributions from other degrees of freedom, i.e. translation, rotation, vibration, and electronic, which were calculated by the standard statistical mechanical method using rigid-rotor harmonic-oscillator approximations, to yield the property values tabulated in tables 3 and 9. The calculated heat capacities and entropies are in agreement with the available experimental values.

2. Propanone

Propanone is an important industrial chemical. Its molecular structure has been investigated by electron diffraction [9–13] and microwave spectroscopy [14]. The results obtained by electron diffraction are not in good agreement. For computation of the product of the three principal moments of inertia, $I_A I_B I_C$, the values of I_A, I_B, and I_C determined by Swalen and Costain [14] were used.

Numerous researchers have observed the infrared [15–25] and Raman [26–34] spectra of propanone. Its fundamental vibrational wavenumbers were derived by many investigators [35–37] by normal-coordinate calculations. Recently, Shimanouchi [38] reviewed the spectral data in the literature and reported a complete set of vibrational assignments for the CH_3COCH_3 molecule. These vibrational wavenumbers were selected for evaluation of the vibrational contributions to the thermodynamic properties of propanone, with the exception of the two torsional frequencies 105 and 109 cm^{-1}, for which the contributions to the thermodynamic properties were evaluated separately. The method of calculation of the internal rotational contributions to the thermodynamic properties for CH_3COCH_3 is described below.

The internal rotational partition function employed in the calculation was formed by summation of the appropriate internal rotational energy levels. The energy levels for each of the two CH_3 tops were generated by use of an internal rotational potential function: $V=\frac{1}{2}V_3(1-\cos 3\theta)$, where V_3=internal rotational barrier height and θ=angle of internal rotation of the CH_3 top. It was assumed that the energy of interaction was negligible. This assumption was found to be valid, insofar as the calculated heat capacities and entropies are in agreement with the experimental values as discussed in section 4.

The internal rotational barrier height (V_3) for the CH_3 top in the CH_3COCH_3 molecule has been determined from microwave [14] and infrared [15] data as 783 ± 40 and 830 ± 30 cal mol^{-1}, respectively, which are in agreement within their experimental uncertainties.

Swalen and Costain [14] developed a theory of internal rotation in molecules with two symmetric rotors attached to a rigid frame with C_{2v} symmetry. They assumed that the potential energy hindering internal rotation arises from the interaction of one of the rotors with the rigid frame and also with the other rotor. Since the latter interaction depends on both internal angles, θ_1 and θ_2, the potential function for each rotor contains cross terms which was called a 'gearing' of the two rotors [14]. The potential energy restricting internal rotation may be written as a Fourier series in θ_1 and θ_2 [15]: $V(\theta_1, \theta_2) = V_0 + \frac{1}{2} V_3 (2 - \cos 3\theta_1 - \cos 3\theta_2) + V_3' \cos 3\theta_1 \cos 3\theta_2 + V_3'' \sin 3\theta_1 \sin 3\theta_2 +$(sixfold and higher terms). In our evaluation of the internal rotational energy levels for each rotor, we made the assumption that the two CH_3 rotors in the CH_3COCH_3 molecule are independent of each other. This was necessary because of the lack of a computer program for generating the internal rotational energy levels using the above potential function in the wave equation, however, according to Swalen and Costain [14], the values of V_3' and V_3'', which are mutual interactions between rotors, are small, of the order of 5 cm^{-1}.

Based on $V_3 = 830$ cal mol^{-1} and the internal rotation constants (F) reported by Fateley and Miller [15], the internal rotational energy levels (up to 17000 cm^{-1})^2 for the two CH_3 tops were evaluated.

In table 2, which summarizes the reported internal rotation parameters, the two torsional frequencies reported by Cossee and Schachtschneider were derived by normal-coordinate calculation. Schumann and Aston selected $V_3 = 1000$ cal mol^{-1} in order to fit the calculated entropy at 329.3 K so as to be consistent with the calorimetric entropy. Adopting V_3 of Schumann and Aston, Pennington and Kobe estimated the value $v_{24} = 200$ cm^{-1} as giving the best fit with the calorimetric data, but this is inconsistent with the spectroscopic results.

Employing the molecular constants listed in table 1, the ideal gas thermodynamic properties, $H° - H_0°$, $-\left(\frac{G° - H_0°}{T}\right)$, $\left(\frac{H° - H_0°}{T}\right)$, $S°$, and $C_p°$ for propanone in the temperature range 0–1500 K and at 1 atm, were calculated by statistical mechanical procedures. The results are presented in table 3.

The enthalpies of combustion ($\Delta Hc°$) for propanone in the liquid and gaseous states have been determined by several investigators [42, 44, 50, 51, 52]. Miles and Hunt [44] employed a constant-pressure flame calorimeter for measurement and obtained $\Delta Hc°$(CH_3COCH_3, g, 298.15 K) = −435.32 ± 0.20 kcal$_{15°C}$ mol^{-1}. This value was corrected for molecular weight (from 1939 Atomic Weights to 1973 Atomic Weights) and calorie unit to − 435.52 kcal mol^{-1} which was used in the calculation of the enthalpy of formation ($\Delta Hf°$) for propanone. The result is shown in table 4. Springall and White [42]

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[2] In keeping with the custom commonly employed in molecular spectroscopy, energy and frequency are expressed in their wavenumber (cm^{-1}) equivalents.

measured the value of ΔHc° (CH_3COCH_3, ℓ, 298.15 K) as −427.9 kcal mol^{-1} which yields ΔHf°(CH_3COCH_3, ℓ, 298.15 K) = − 59.20 kcal mol^{-1}. By use of ΔHv° (298.15 K) = 7.40 kcal mol^{-1} [1], the enthalpy of formation for propanone (g) at 298.15 K was obtained as − 51.80 kcal mol^{-1}. For these calculations, the values, ΔHf° (CO_2, g, 298.15 K) = −94.051 kcal mol^{-1} and ΔHf° (H_2O, ℓ, 298.15 K) = − 68.315 kcal mol^{-1} [54], were used. It is interesting to note that the above two ΔHf°(CH_3COCH_3, g, 298.15 K) values are the only two recent calorimetric measurements available in the present literature. More calorimetric measurements for this important compound, using the modern high precision calorimetric technique, are needed.

Numerous research studies have been done on the chemical equilibria of hydrogenation of propanone [41, 45, 47, 49, 53] to form 2-propanol and for the reverse reaction, dehydrogenation of 2-propanol [43, 46, 48] to give propanone and hydrogen. From the equilibrium constants obtained, the investigators derived the enthalpy changes for these reactions by the second-law method. Some of the typical results are shown in table 4. Based on these ΔHr° values, we evaluated the values of ΔHf°(CH_3COCH_3, g, 298.15 K) which are given in the last column of that table. In these calculations the value of ΔHf°((CH_3)$_2$CHOH, g, 298.15 K), −65.11 kcal mol^{-1}, was taken from [55]. Based on the ΔHf° (CH_3COCH_3, g, 298.15 K) values listed in table 4, we adopted the value, −51.90 ± 0.12 kcal mol^{-1} [83], as the best value and used it in this study

Employing the ΔHf°(CH_3COCH_3, g, 298.15 K) and the thermodynamic functions for propanone (g) from this work and those for C(graphite), H_2(g), O_2(g) from [56], the values of ΔHf°, ΔGf°, and log Kf in the temperature range 0–1500 K and at 1 atm were calculated. The results are presented in table 3.

3. 2-Butanone

The rotational isomerism of 2-butanone (g) has been investigated by infrared spectroscopy and electron-diffraction by Shimanouchi, Abe, and Mikami [57] and Abe, Kuchitsu, and Shimanouchi [64], respectively. Their results showed that 2-butanone has *trans* and *gauche* conformations; however, the *trans* isomer is far more stable than the *gauche* form. In view of this fact, the molecular structure of *trans*-2-butanone was selected for evaluation of the thermodynamic properties for 2-butanone in the ideal gaseous state.

Romers and Creutzberg [9] and Abe, et al. [64] have elucidated the molecular structure of *trans*-2-butanone by use of the electron diffraction method. The structural parameters reported by Romers and Creutzberg were used for calculating the product of the three principal moments of inertia as given in table 7. The three internal rotational constants for the CH_3, CH_3 in C_2H_5, and C_2H_5 tops were obtained as 5.8201, 5.4682, and 1.0681 cm^{-1}, respectively.

The infrared [16, 30, 57, 58, 60, 61, 76, 77] and Raman [16, 30, 62, 63, 78, 79, 80] spectra have been reported for this compound by many investigators. Shimanouchi [38] critically reviewed the reported infrared and Raman spectra and the related theoretical calculations for 2-butanone and gave a complete set of vibrational assignments for this compound. This vibrational assignments, ν_1 through ν_{30}, were adopted for evaluation of the vibrational contributions to the thermodynamic properties of 2-butanone.

TABLE 1. Molecular constants for propanone

Molecular weight	58.0798
Point group	C_{2v}
Symmetry number	18
Ground state configuration	$^1A_1$
Product of the three principal moments of inertia, g^3 cm^6	1.39188 × 10^{-114}
Internal rotational constant, cm^{-1}	5.931 for b_1 species 5.517 for a_2 species
Torsional frequency, cm^{-1}	108 for b_1 species 105 for a_2 species
Potential barrier height, cal mol^{-1}	830, 830
Vibrational wavenumbers, cm^{-1}	a_1: 3019, 2937, 1731, 1435, 1364, 1066, 777, 385; a_2: 2963, 1426, 877; b_1: 3019, 2937, 1410, 1364, 1216, 891, 530; b_2: 2972, 1454, 1091, 484.

TABLE 2. Summary of reported torsional frequencies and potential barriers to internal rotation in propanone

Torsional frequency, cm^{-1}		V_3 cal mol^{-1}	Investigator (year)	Reference
ν_{12}	ν_{24}			
105	105		Cossee and Schachtschneider (1966)	[35]
		757.1 ± 0.5	Peter and Dreizler (1965)	[39]
105	109 ± 2	830 ± 30	Fateley and Miller (1962)	[15]
	95		Möller (1960)	[21]
		783 ± 40	Swalen and Costain (1959)	[14]
	200	1000	Pennington and Kobe (1957)	[1]
		1000	Schumann and Aston (1938)	[40]
105.3	108.4	830	This work	

TABLE 3. Ideal gas thermodynamic properties for propanone

T	$H^\circ - H^\circ_0$	$-\frac{(G-H^\circ_0)}{T}$	$\frac{(H^\circ-H^\circ_0)}{T}$	S°	C°_p	ΔHf°	ΔGf°	log Kf
K	cal mol^{-1}	cal K^{-1} mol^{-1}				kcal mol^{-1}		
0	0	0	0	0	0	−47.92	−47.92	infinite
50	429	38.91	8.58	47.49	10.06	−49.18	−47.50	+207.619
100	991	45.29	9.91	55.20	12.06	−49.60	−45.66	+99.793
150	1621	49.49	10.81	60.29	13.14	−50.09	−43.59	+63.513
200	2308	52.70	11.54	64.24	14.41	−50.67	−41.34	+45.173
273.15	3448	56.45	12.62	69.08	16.85	−51.59	−37.79	+30.239
298.15	3881	57.58	13.02	70.59	17.81	−51.90	−36.50	+26.757
300	3914	57.66	13.05	70.70	17.88	−51.92	−36.40	+26.521
400	5904	61.64	14.76	76.40	21.93	−53.11	−31.05	+16.962
500	8294	65.13	16.59	81.72	25.78	−54.14	−25.41	+11.107
600	11050	68.32	18.41	86.72	29.17	−55.00	−19.58	+7.133
700	14110	71.29	20.16	91.45	32.10	−55.70	−13.62	+4.252
800	17450	74.09	21.82	95.90	34.64	−56.25	−7.57	+2.068
900	21030	76.75	23.37	100.11	36.83	−56.68	−1.46	+0.353
1000	24810	79.28	24.81	104.09	38.73	−56.98	+4.71	−1.030
1100	28770	81.71	26.15	107.86	40.37	−57.19	+10.85	−2.157
1200	32880	84.04	27.40	111.44	41.80	−57.32	+17.08	−3.110
1300	37120	86.28	28.55	114.84	43.04	−57.39	+23.27	−3.912
1400	41480	88.44	29.63	118.06	44.11	−57.41	+29.51	−4.609
1500	45940	90.52	30.62	121.14	45.04	−57.39	+35.70	−5.202

1 cal = 4.184 J.

TABLE 4. Enthalpies of reaction and formation at 298.15 K for propanone[a]

ΔHr° kcal mol^{-1}	Experimental method	Investigator (year)	ΔHf°(g) kcal mol^{-1}
−13.20 ± 0.10	equilibrium study	Buckley and Herington (1965)[b]	−51.91 ± 0.16
−427.9 ± 0.20	bomb calorimetry	Springall and White (1954)[c]	−51.80 ± 0.21
13.98 ± 0.20	equilibrium study	Kobb and Burwell (1945)[d]	−51.60 ± 0.25
−435.52 ± 0.20	flame calorimetry	Miles and Hunt (1941)[e]	−51.58 ± 0.21
−13.29 ± 0.10	equilibrium study	Dolliver, et al. (1938)[f]	−51.82 ± 0.17
14.50 ± 0.20	equilibrium study	Parks and Kelley (1928)[g]	−50.61 ± 0.25
−431.0 ± 0.50	bomb calorimetry	Emery and Benedict (1911)[h]	−48.70 ± 0.60
−436.45 ± 0.80	bomb calorimetry	Thomsen (1905)[i]	−50.65 ± 0.90
−427.0 ± 1.00	bomb calorimetry	Delepine (1900)[j]	−52.70 ± 1.20

[a] The value of ΔHf°(g, 298.15 K) adopted in this work is −51.90 ± 0.12 cal mol^{-1}.

[b] Reference [41]; chemical reaction: $(CH_3)_2CO(g) + H_2(g) = (CH_3)_2CHOH(g)$.

[c] Reference [42]; chemical reaction: $(CH_3)_2CO(\ell) + 4\ O_2(g) = 3\ CO_2(g) + 3\ H_2O(\ell)$;
$\Delta Hv^\circ(CH_3COCH_3,\ \ell,\ 298.15\ K) = 7.40$ kcal mol^{-1}.

[d] Reference [43]; chemical reaction: $(CH_3)_2CHOH(g) = (CH_3)_2CO(g) + H_2(g)$.

[e] Reference [44]; chemical reaction: $(CH_3)_2CO(g) + 4\ O_2(g) = 3\ CO_2(g) + 3\ H_2O(\ell)$.

[f] Reference [45]; chemical reaction: same as b.

[g] Reference [46]; chemical reaction: same as d.

[h] Reference [50]; chemical reaction: same as c.

[i] Reference [51]; chemical reaction: same as e.

[j] Reference [52]; chemical reaction: same as e.

In order to calculate the internal rotational contributions to thermodynamic properties of $CH_3COCH_2CH_3$, it was necessary to evaluate the three internal rotational barrier heights for the three tops, namely CH_3, CH_3 in C_2H_5, and C_2H_5, in this molecule. Sinke and Oetting [4] selected two methyl barriers as 1200 and 2950 cal mol^{-1} (see table 8). They adopted the skeletal rotational potential function for the ethyl rotor similar to that used by Nickerson et al. [5], i.e., the potential function shows three minima per cycle of internal rotation with two equal minima higher than the third. Nickerson et al. adopted a model of an equilibrium between rotational isomers in which the barrier for rotation of the *trans* form was assumed to be 1000 cal mol^{-1}, the energy of the *trans* to *gauche* (skew) reaction was assumed to be 700 cal mol^{-1} plus the value of 600 cal mol^{-1} for the attractive force between oxygen and the extended methyl group. This model gave the best fit between the calculated and experimental heat capacities [5].

In our study we used the three barrier heights shown in table 8, together with the three internal rotational constants mentioned previously, for calculation of the internal rotational energy levels for each of the three rotors in the $CH_3COCH_2CH_3$ molecule. The three sets of internal rotational energy levels (101 levels up to 14600 cm^{-1} for CH_3, 45 levels up to 10000 cm^{-1} for CH_3 in C_2H_5, and 180 levels up to 9100 cm^{-1} for C_2H_5) thus obtained were employed for evaluation of the thermodynamic properties due to internal rotation for 2-butanone. The value of the first barrier height listed in table 8 was taken to be the same as that in CH_3COCH_3 molecule. Those for the other two barrier heights were chosen as fitting parameters to yield the best fit between the calculated C_p° and S° values and the experimental data. The calculated torsional frequencies are consistent with those vibrational assignments in [38], except for the value for ν_{33} (see table 8).

Based on the selected molecular constants shown in tables 7 and 8, the thermodynamic functions for 2-butanone were calculated by standard statistical mechanical procedures, using rigid-rotor and harmonic-oscillator approximations. The results are presented in table 9.

The value of ΔHf° ($CH_3COC_2H_5$,g,298.15 K) was selected from results of calorimetric measurements [4, 42, 65, 67, 68, 69] and chemical equilibrium studies [41, 43, 45, 66] as -57.02 ± 0.20 kcal mol^{-1}, which is in consistency with the value given in [83]. The reported enthalpies of reactions (ΔHr°) by investigators and the derived enthalpies of formation (ΔHf°) for 2-butanone

TABLE 5. Comparison of calculated and measured heat capacities for propanone[a]

T	C_p	$C_p - C_p^{\circ b}$	C_p°		C_p° (calc.) −
K			Experimental	Calculated	C_p° (expt.)
Pennington and Kobe (1957)[c]					
338.2	20.13	0.74	19.39	19.41	0.02
371.2	21.17	0.37	20.80	20.76	− 0.04
405.2	22.39	0.21	22.18	22.14	− 0.04
439.2	23.69	0.13	23.56	23.49	− 0.07
Collins, Coleman and de Vries (1949)[d]					
334	21.80	2.45	19.35	19.24	− 0.11
348	21.70	1.77	19.93	19.81	− 0.12
363	22.10	1.30	20.80	20.43	− 0.37
378	22.30	0.97	21.33	21.04	− 0.29
393	22.70	0.75	21.95	21.65	− 0.30
408	23.10	0.59	22.51	22.25	− 0.26
428	24.20	0.44	23.76	23.05	− 0.71
438	24.40	0.38	24.02	23.44	− 0.58
332.6	21.80	2.54	19.26	19.19	− 0.07
347.8	21.70	1.78	19.92	19.81	− 0.11
372.3	22.00	1.08	20.92	20.81	− 0.11
422.6	23.60	0.47	23.13	22.87	− 0.26
Benniwitz and Rossner (1938)[e]					
410.2			22.50	22.36	− 0.14

[a] Unit = cal K^{-1} mol^{-1}; 1 cal = 4.184 J.

[b] Derived from data on second virial coefficients, see text for details.

[c] The C_p values were measured at $P = 1/3$ atm; reference [1].

[d] The first 8 data points were measured using reverse-flow calorimeter and the remaining 4 data points were measured using direct-flow calorimeter; reference [70].

[e] Reference [71].

TABLE 6. Comparison of calculated and experimental entropies for propanone

$\frac{T}{\mathrm{K}}$		$S°$ cal K^{-1} mol^{-1}
	Third-law entropy	
0.00– 17.77	Extrapolation	0.667
17.77–126.00	Integration—Crystal II	17.778
126.00	Transition (10.0/126.00)	0.079
126.00–178.50	Integration—Crystal I	6.871
178.50	Fusion (1380.0/178.50)	7.731
178.50–298.15	Integration—liquid	14.676
	$S°$ (ℓ, 298.15 K)	47.80 ± 0.20 [a]
	Vaporization	24.83 [b]
	Compression	−2.38 [b]
	Gas imperfection	0.22 [b]
	$S°$(g, 298.15 K)	70.47 ± 0.25
	Statistical entropy	
298.15	Pennington and Kobe (1957) [b]	70.49 ± 0.3
329.3	Schumann and Aston (1938) [c]	72.7 ± 0.5
298.15	This work	70.59
329.3	This work	72.42

[a] Reference [74].
[b] Reference [1].
[c] Reference [40].

(g) are summarized in table 10. The values of $\Delta Hf°$ (g) calculated from the combustion bomb calorimetric measurements by Sinke and Oetting [4] and the dehydrogenation of 2-butanol (g) equilibrium study by Buckley and Herington [41] are in good agreement. However, the $\Delta Hf°$ (g) values evaluated from the other reported $\Delta Hr°$ are not in accord. Since liquid 2-butanone samples were used in the combustion experiments, the value $\Delta Hv°$ ($CH_3COC_2H_5$,ℓ,298.15 K) = 8.30 kcal mol^{-1} [5] was employed to convert the $\Delta Hf°$ ($CH_3COC_2H_5$, ℓ,298.15 K) to $\Delta Hf°$ ($CH_3COC_2H_5$,g,298.15 K). Crog and Hunt measured the enthalpy of combustion ($\Delta Hc°$) for 2-butanone (g) by flame calorimetry [67]. They corrected the $\Delta Hc°$ value obtained for gas to that for liquid by subtraction of $\Delta Hv°$ (298.15 K) and reported $\Delta Hc°$ ($CH_3COC_2H_5$,ℓ,298.15 K) to be -582.28 ± 0.37 $\mathrm{kcal}_{15°\mathrm{C}}$ mol^{-1}. This $\Delta Hc°$ value was recalculated to be -582.55 ± 0.37 kcal mol^{-1} after corrections for molecular weight and the unit for calorie.

For evaluation of $\Delta Hf°$ (g, 298.15 K) for 2-butanone from the reported second law values of the enthalpies of dehydrogenation of 2-butanol (g) and hydrogenation of 2-butanone (g), a value of $\Delta Hf°$ ($CH_3CHOHC_2H_5$, g,298.15 K) = − 69.94 kcal mol^{-1} [55] was used. Based on the selected $\Delta Hf°$ ($CH_3COC_2H_5$,g,298.15 K) and the thermodynamic functions for C (graphite), H_2 (g), O_2 (g) from [56] and those for 2-butanone (g) from this work, the thermodynamic properties $\Delta Hf°$, $\Delta Gf°$, and log Kf in the temperature range from 0 to 1500 K and at 1 atm were calculated and are given in table 9.

TABLE 7. Molecular constants for 2-butanone

Molecular weight	72.1074
Point group	C_s
Symmetry number	9
Ground state configuration	$^1A'$
Product of the three principal moments of inertia, g^3 cm^6	6.5461×10^{-114}
Vibrational wavenumbers, cm^{-1}	a': 2983(2), 2910(2), 2884, 1716, 1460, 1422, 1413, 1373, 1346, 1263, 1182, 1089, 997, 939, 760, 590, 413, 260; a'': 2983(2), 2941, 1460, 1413, 1263, 1108, 952, 768, 460

4. Discussion

Pennington and Kobe [1] determined the vapor heat capacities of propanone as a function of pressure, from $\frac{1}{3}$ to $\frac{5}{3}$ atm, and at four temperatures, namely 338.2, 371.2, 405.2, and 439.2 K. The C_p values measured at $\frac{1}{3}$ atm are listed in table 5. Employing the second virial coefficients for propanone from [56], the limiting values of $(\partial C_p/\partial P)_T$ at zero pressure at the above four temperatures were calculated. From the $(\partial C_p/\partial P)_T$ values thus obtained, the heat capacity difference between the real gas and the ideal gas at the same given temperature, $C_p - C_p°$, was evaluated. The results are presented in table 5. The difference between the measured C_p and the calculated $C_p - C_p°$ is $C_p°$, the heat capacity of 2-butanone at zero pressure or in the ideal gaseous state. These $C_p°$ values are compared with those obtained in this work in table 5. The differences in $C_p°$ (experimental) and $C_p°$ (calculated) are within the experimental uncertainty which was estimated as ± 0.2 % [1]. Collins, Coleman, and de Vries [70] measured the heat capacities for 2-butanone (g) at 1 atm, 332.6–438 K, by use of both direct-flow and reverse-flow calorimeters. Adopting the same procedure, the experimental $C_p°$ values were derived and are compared with our calculated ones in table 5. However, the differences are far larger than the experimental errors. This is also true for the comparison between our statistically calculated $C_p°$ at 410.2 K and that reported by Bennewitz and Rossner [71], as shown in the same table. The heat capacities reported by Wiedmann [72] and Regnault [73] are only of historical interest and were not adopted for comparison.

The third-law entropy of 2-butanone (g) at 298.15 K was evaluated [74] as 70.47 ± 0.25 cal K^{-1} mol^{-1} (see table 6 for details) which is in agreement with our statistically calculated entropy value 70.59 cal K^{-1} mol^{-1}. It is interesting to note that the entropies re-

TABLE 8. Torsional frequencies and potential barriers to internal rotation in 2-butanone

Barrier height, cal mol^{-1}			Torsional frequency, cm^{-1}			Investigator (year)	Reference
V_3(CH$_3$)	V_3(CH$_3$ in C$_2$H$_5$)	V(C$_2$H$_5$)	ν_{32}	ν_{31}	ν_{33}		
1200	2950	1260 (V_1)^a 1260 (V_2)				Sinke and Oetting (1964)	[4]
1000	2400	^{b}				Nickerson, et al. (1961)	[5]
			106	201	87	Shimanouchi (1972)	[38]
830	2620	1910 (V_1) 955 (V_3)^c	108	200	62	This work	

[a] V_1 = height of the lower barrier, V_2 = the potential energy at the higher minima, $V_1 + V_2$ = height of the higher barrier.

[b] See text.

[c] The potential function: $V = \frac{1}{2}V_1(1-\cos\theta) + \frac{1}{2}V_3(1-\cos 3\theta)$ where θ = angle of internal rotation.

TABLE 9. Ideal gas thermodynamic properties for 2-butanone

T	$H^\circ - H^\circ_0$	$-\frac{(C - H^\circ_0)}{T}$	$\frac{(H^\circ - H^\circ_0)}{T}$	S°	C°_p	ΔHf°	ΔGf°	log Kf
K	cal mol^{-1}	cal K^{-1} mol^{-1}				kcal mol^{-1}		
0	0	0	0	0	0	−51.89	−51.89	infinite
50	453	42.77	9.06	51.84	10.90	−53.63	−51.13	+223.469
100	1086	49.61	10.86	60.47	14.34	−54.25	−48.38	+105.733
150	1882	54.34	12.55	66.88	17.43	−54.89	−45.31	+66.014
200	2819	58.16	14.10	72.26	20.00	−55.58	−42.01	+45.904
273.15	4408	62.86	16.14	79.00	23.46	−56.66	−36.89	+29.515
298.15	5010	64.31	16.80	81.11	24.68	−57.02	−35.04	+25.689
300	5056	64.41	16.85	81.26	24.78	−57.05	−34.90	+25.428
400	7787	69.62	19.47	89.08	29.87	−58.44	−27.31	+14.919
500	11020	74.24	22.04	96.28	34.72	−59.64	−19.39	+8.474
600	14710	78.48	24.52	103.00	39.02	−60.63	−11.24	+4.095
700	18800	82.43	26.86	109.30	42.75	−61.43	−2.94	+0.917
800	23250	86.17	29.06	115.22	46.00	−62.05	+5.46	−1.492
900	27990	89.71	31.10	120.81	48.82	−62.51	+13.93	−3.383
1000	33000	93.08	33.00	126.08	51.26	−62.81	+22.46	−4.909
1100	38230	96.31	34.76	131.07	53.39	−62.98	+30.95	−6.149
1200	43670	99.41	36.39	135.80	55.23	−63.06	+39.53	−7.199
1300	49270	102.38	37.90	140.28	56.82	−63.07	+48.07	−8.082
1400	55020	105.24	39.30	144.54	58.21	−63.01	+56.66	−8.846
1500	60910	108.00	40.60	148.60	59.41	−62.90	+65.19	−9.498

1 cal = 4.184 J.

ported by Pennington and Kobe at 298.15 K and Schumann and Aston [40] at 329.3 K were obtained by using estimated missing molecular and spectroscopic data. Therefore, the agreement between their values and the experimental third-law entropies are fortuitous.

The vapor heat capacities of 2-butanone in the temperature range 347.15 to 467.15 K and at pressures 0.248–1.709 atm were measured by Nickerson, Kobe, and McKetta [5]. By use of the same procedure as described previously for propanone, the $C_p{}^\circ$ (experimental) values for 2-butanone (g) were calculated. These experimental $C_p{}^\circ$ values compare favorably with the statistically calculated values in this work. Again, heat capacity reported by Bennewitz and Rossner [71] is not consistent with our value. The above results are presented in *table 11*.

TABLE 10. Enthalpies of reaction and formation at 298.15 K for 2-butanone [a]

$\Delta Hr°$ kcal mol^{-1}	Experimental method	Investigator (year)	$\Delta Hf°$(g) kcal mol^{-1}
12.95±0.16	equilibrium study	Buckley and Herington (1965) [b]	−56.99±0.29
−584.17±0.27	bomb calorimetry	Sinke and Oetting (1964) [c]	−57.01±0.29
−582.8±0.20	bomb calorimetry	Springall and White (1954) [d]	−58.36±0.21
−582.8±0.20	bomb calorimetry	Parks, et al. (1950) [e]	−58.36±0.25
12.96±0.20	equilibrium study	Cubberley and Mueller (1946) [f]	−56.98±0.24
13.66±0.20	equilibrium study	Kolb and Burwell (1945) [g]	−56.28±0.25
−582.55±0.37	flame calorimetry	Crog and Hunt (1942) [h]	−58.61±0.38
−582.59±0.20	bomb calorimetry	Moore, et al. (1940) [i]	−58.57±0.21
−13.19±0.26	equilibrium study	Dolliver, et al. (1938) [j]	−56.98±0.27
−582.3 ±0.50	bomb calorimetry	Swietoslawski (1920) [k]	−58.86±0.60

[a] The value of $\Delta Hf°$(g, 298.15 K) adopted in this work is −57.02±0.20 kcal mol^{-1}.

[b] Reference [41]; chemical reaction: $CH_3CHOHC_2H_5(g) = CH_3COC_2H_5(g) + H_2(g)$.

[c] Reference [4]; chemical reaction: $CH_3COC_2H_5(\ell) + 5.5\ O_2(g) = 4\ CO_2(g) + 4\ H_2O(\ell)$.

[d] Reference [42]; chemical reaction: same as c.

[e] Reference [65]; chemical reaction: same as c.

[f] Reference [66]; chemical reaction: same as b.

[g] Reference [43]; chemical reaction: same as b.

[h] Reference [67]; chemical reaction: same as c. The listed $\Delta Hr°$ value was converted from $\Delta Hr°$(g, 298.15 K).

[i] Reference [68]; chemical reaction: same as c.

[j] Reference [45]; chemical reaction: $CH_3COC_2H_5(g) + H_2(g) = CH_3CHOHC_2H_5(g)$.

[k] Reference [69]; chemical reaction: same as c.

TABLE 11. Comparison of calculated and measured heat capacities for 2-butanone [a]

T	C_p	$C_p - C_p^{\circ}$ [b]	C_p°		C_p°(calc.) −
K			Experimental	Calculated	C_p°(exptl.)
			Nickerson, Kobe, and McKetta (1961) [c]		
347.15	27.63	0.42	27.21	27.16	−0.05
372.15	28.75	0.27	28.48	28.45	−0.03
397.15	29.91	0.19	29.72	29.72	0.00
432.15	31.57	0.12	31.45	31.48	+0.03
467.15	33.19	0.08	33.11	33.18	0.07
			Bennewitz and Rossner (1938) [d]		
410.2			29.80	30.39	0.59

[a] Unit = cal K^{-1} mol^{-1}; 1 cal = 4.184 J.

[b] Derived from data on second virial coefficients, see text for details.

[c] The C_p values were measured at $P = 0.248$ atm; reference [5].

[d] Reference [71].

Table 12 gives the comparison of calculated and experimental entropies for 2-butanone (g). The entropy at 298.15 K obtained in this work is in reasonable agreement with the third-law entropy value reported in [74].

The ideal gas thermodynamic properties for 2-butanone have been reported by Nickerson, Kobe, and McKetta [5] and Sinke and Oetting [4]. In their calculations, they used the spectroscopic data available at that time. For evaluation of the internal rotational contributions, Nickerson et al. used the tables of Pitzer and Gwinn [81], while Sinke et al. adopted the tables published by Scott and McCullough [82]. In this work, we selected the best values of molecular and spectroscopic constants available today. We generated internal rotational energy levels and used a potential function by summation of these energy levels for calculation of the internal rotational contributions to thermodynamic properties for each of the three rotating tops in the $CH_3COCH_2CH_3$ molecule. Our method produces more reliable values than those reported previously. Of course, in the present calculation, an assumption was made that the three tops in the molecule are independent of each other.

TABLE 12. Comparison of calculated and experimental entropies for 2-butanone

$\frac{T}{\text{K}}$		S° cal K^{-1} mol^{-1}
	Third-law entropy	
0.00 – 11.10	Extrapolation	0.245
11.10 – 186.505	Integration – Crystal	29.051
186.505	Fusion (2004.0/186.505)	10.745
186.505 – 298.15	Integration – liquid	17.097
	S° (ℓ, 298.15 K)	57.14 ± 0.15 [a]
	Vaporization	27.87 [b]
	Compression	−4.23 [b]
	Gas imperfection	0.15 [b]
	S° (g, 298.15 K)	80.93 ± 0.20
	Statistical entropy	
298.15	Andon, et al. (1968) [c]	80.83 ± 0.20
298.15	Sinke and Oetting (1964) [d]	80.81 ± 0.20
298.15	Nickerson, et al. (1961) [b]	82.51 ± 0.60
298.15	This work	81.11

[a] Reference [74].

[b] Reference [5]; according to Sinke and Oetting [4], the reported entropy value was incorrect due to some mathematical errors involved in calculation, the correct value should be 80.91 cal $\text{K}^{-1}\text{mol}^{-1}$.

[c] Reference [75]; the S° value was derived from low temperature C_p measurements.

[d] Reference [4].

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